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CANADIAN CONTRIBUTION TO IEA, TASK IV, PRODUCTION OF HYDROGEN BY PHOTOCATALYTIC WATER ELECTROLYSIS - 1985

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Semiconductor Materials for PEC and Catalytic Processes

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by

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ABSTRACT

This report presents a summary of work carried out at CANMET during 1985, under the auspices of the International Energy Agency, Task VI Program of Research and Development on the Production of Hydrogen by Photocatalytic Water Electrolysis. In-house work on the semiconductor and photo-electrochemical proportions and impedance measurements of specular hematite, and luminescence spectroscopic studies of semiconductor electrodes have been reported. The report also includes a summary of contract work carried out at Simon Fraser University, Burnaby, B.C. The contract work includes studies on the oxidation of organics by holes on semiconductor (TiO_2 and SnO_2) surfaces by the current doubling technique.

CONTRIBUTION CANADIENNE À L'AIE, PROJET DE TRAVAIL IV, PRODUCTION D'HYDROGÈNE PAR ÉLECTROSE PHOTOCATALYTIQUE DE L'EAU - 1985

par

S.M. Ahmed

RÉSUMÉ

Le rapport comprend un bref exposé des travaux effectués au CANMET au cours de l'année 1985 sous les auspices de l'Agence internationale de l'énergie, Projet de travail lV, Programme de recherche et développement sur la production d'hydrogène au moyen de l'électrolyse photocatalytique de l'eau. Il porte également sur les travaux de recherche internes sur le semi-conducteur et les proportions photo-électrochimiques et sur la mesure de l'impédance de l'hématite spéculaire et les études de la luminescence spectroscopique des électrodes semi-conducteurs. Un sommaire des travaux effectués à forfait à l'université Simon Fraser, Burnaby (B.C.) est également présenté. Ces travaux comprenaient des études sur l'oxydation des matières organiques qui se produit par l'intermédiaire des trous à la surface du semi-conducteur (TiO_2 et SnO_2) au moyen de la technique de doublage du courant.

CANADIAN CONTRIBUTION TO IEA, TASK VI
PROGRAMME OF RESEARCH AND DEVELOPMENT ON PRODUCTION
OF HYDROGEN BY PHOTOCATALYTIC WATER ELECTROLYSIS-1985

Project Leader: S.M. Ahmed, Canada Centre for Mineral and Energy Technology Department of Energy, Mines and Resources, Ottawa, Ontario, Canada.

Consultant: Professor, S.R. Morrison, Director, Energy Research Institute, Simon Fraser University, Burnaby, British Columbia, Canada.

I. Summary of Work in Progress at CANMET, Ottawa, Ontario.

1. Photoelectrochemistry of Specular Hematite:

Participating Scientists: S.M. Ahmed and J. Leduc

Naturally occurring specular hematite, (Québec, Canada) containing 0.6 mass % of Ti, was found to be a degenerate semiconductor which yielded negligible photocurrents (i_{ph}) when tested as a photoanode in a photoelectrolytic cell. The obvious cause for the somewhat metallic behaviour appeared to be slight reduction of the hematite in nature. As expected, when reoxidized by heating in air at 900°C for 1h or more, the carrier concentration decreased in the surface layers and the photocurrents increased substantially. The PEC properties of specular hematite electrodes after reoxidation have been investigated by studying (i_{ph}-V) behaviour, photocurrent spectra and impedance measurements. The photon conversion efficiencies (ℓ_{ph}) were determined and were still found to be low. In contrast to other photoanodes, the ℓ_{ph}

shows a continuous increase with increasing photon energies in the uv range. A possible cause appears to be the presence of a series of discrete energy levels in the valence band structure of specular hematite and the presence of a strong internal magnetic field due to the antiferromagnetic arrangement of uncoupled electrons that the photoexcited electrons have to overcome.

In the longer wave length region ($E>E_g=2.23$eV or $\lambda>563$nm) a tail of photocurrents was observed indicating presence of deep donor levels. Photocurrents obtained by sub-band gap illumination revealed presence of deep donor levels at 0.41 eV and 0.61 eV below the conduction band edge, which also act as trapping centres.

The lower level (0.61eV) appears to be intrinsic in nature and corresponds to slow traps and the upper one is probably due to Ti present and corresponds to traps 20,000 times faster than the first. The density of these trapping centres is being determined. As discussed below, photoelectrochemical luminescence spectroscopy also revealed presence of these centres participating in radiative recombination of the photoexcited electrons.

Attempts are being made to improve the solid state properties of this material by eliminating or reducing the density of these trapping centres.

2. <u>Studies of Semiconductor Surfaces by PEC Luminescence Spectroscopy</u>:
Participating Scientists: S.M. Ahmed and J. Trudel

Equipment has been constructed for studying PEC luminescence

of the semiconductor electrodes. The luminescence spectroscopy is expected to provide information on the radiative recombination processes occurring in the space charge region resulting from the defect structure, trapping centres or localized surface states. The equipment consists of four main parts: (1) An electrochemical system consisting of a recording potentiostat, potential scanner and an especially designed electrochemical cell with an optically flat quartz window to hold the sample; (2) An optical system consisting of a He-Cd laser (442 nm and 325 mn), an He-Ne laser (633 nm), a motor driven Jarrel Ash monochromator, and condensing and focussing optical elements mounted on a vibration free optical bench; (3) A measuring system consisting of a sensitive water cooled PMT, a chopper and a lockin amplifier and a three channel measuring and plotting system (Hewlett Packard #7090A); (4) A computer system (H.P. #9817, with a double disc drive) for partial control and data analysis.

Results:

Preliminary studies have been conducted with GaAs, GaAs with cobalt films and specular hematite electrodes.

The photoluminescence of the free-surface of the n-type, Si-doped GaAs samples shows a single peak at 690 nm (1.80 eV); the position of this peak is unaltered by the electrical polarisation of the cell but its intensity and the high energy sideband are affected by these factors. This peak is more energetic than the band gap of GaAs (1.43 eV at 300K) and its nature can only be defined by further studies.

The spectrum of the cobolt-plated (10nm) n-GaAs:Si samples shows more peaks with the 690 nm present only for the pH 13.0 electrolyte; the additional peaks, at 622 and 682 nm, behave in a complex manner with respect to the electrolyte and to the polarisation of the cell.

The specular hematite samples have only recently been studied by photoluminescence and they show a single peak at 667 nm; its behaviour under different conditions of ph and electrical polarisation has not yet been studied. However, within experimental error, this peak seems to correspond to a similar peak found in the photocurrent spectrum of specular hematite under sub-bandgap illumination, that was assigned to a deep donner level acting as a trapping centre.

Publications:

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3. J. Trudel and S.M. Ahmed, Laser Luminescence studies of Semiconductor for Surfaces-In Prepn.
4. S.M. Ahmed and J. Leduc "Photoelectrochemical Behaviour of n-GaAs with Cobalt Films". Presented at the Electrochemical Soc., Fall Meeting, Las Vegas, Oct. 13-18, 1985. Extended Abs., 85-2 Abs. No.341 P.515.

II. Summary of Work at Simon Fraser Energy Research Institute, Simon Fraser University, Burnaby, B.C., Canada. V5A 1S6

Electrochemical Research on Oxidation Processes on Semiconductors

Principle Scientist: S. Roy Morrison

The use of semiconductor electrodes is not only important insofar as conversion of solar energy is concerned but also offers the possibility of highly selective electrosynthesis using holes or electrons from semiconductors as reactants in solution. Our emphasis has been in oxidation processes where we are studying the reactions of holes from wide bandgap semiconductors (TiO_2, SnO_2) to oxidize organic species in solution or, more importantly, to generate radicals which, in turn, can initiate chain reactions to form desirable products.

To date most of our studies have emphasized the use of current doubling to monitor the reactions of radical cations produced by oxidation by holes from TiO_2. In the current doubling process a radical produced by hole oxidation of an organic species is detected by the injection of an electron into the conduction band of the semiconductor electrode. The electron injection first demonstrates that the hole is oxidizing the added organic. Second, by noting the efficiency of the electron injection, we can deduce whether secondary reactions of the radical occur whereby the electron is lost and cannot be injected into the semiconductor.

We have found that all alcohols tested provide reactive radicals upon oxidation, triethylamine and ethylene glycol current double, and water, formic acid, ferrocene and dimethyl

formamide all lead to modest current doubling. On the other hand, acetic acid, acetone, ethyl acetate, acrylamide, toluene, phenol, napthalene, dichloromethane, pentene, and acetaldehyde do not show current doubling and thus the radicals formed, either are not injecting electrons into the TiO_2 conduction band or react otherwise.

We have found the acidity of the solvent, apparently, has a strong influence on the reactivity of the resulting radical. As the solvent becomes more basic the current doubling approaches closer to the ideal factor of 2. In this test we have studied trifluoromethane sulfonic acid, dichloromethane, acetonitrile, acetone, water and dimethyl formamide as solvents.

When another reducing agent which does not current double is added to the solution containing a current doubling species such as methanol, two possible complications can ensue: either the hole can directly oxidize the added species or the radical from the methanol can oxidize the added non-current doubling species. If we assume that a reaction between the radical and the non-current doubling species does not occur, then we can immediately analyze a titration curve to give the relative capture cross-sections. By this it is found that most alcohols have a capture cross-section similar to methanol (within a factor of 2) whereas some non-current doubling species have significantly higher cross-sections: the cerous ion has about 1600, the ferrous ion about 4, the thianthrene molecule about 100 times the capture cross-section of methanol. Such information when confirmed by chemical measurements will allow

a detailed knowledge about the preferred reaction route with two or more species in solution.

If two organic species are added together in solution the reaction can again be partially analyzed by the effect on current doubling. For example, in studies of current doubling due to methanol, we find acetaldehyde, acetic acid, acetone, and dichloromethane have no effect. This suggests that these species are not oxidized with methanol present and do not get involved in the reaction. On the other hand, dimethyl formamide and triethylamine significantly lower the current doubling associated with methanol indicating that they preferentially capture holes from the methanol. Third, butanol, formic acid, water, and ethylene glycol all show significantly higher current doubling when added to the methanol (which already has quite high current doubling). This suggests a cooperative interaction between the methanol and these species to enhance the reactivity or lifetime of the radical. These details of this cooperative interaction must be investigated further.

Finally, we have studied the behaviour with different oxidizing agents. The oxidizing agent studied mostly has been dissolved oxygen with the radical depended substantially on the doping of the semiconductor. Apparently, the injection of electrons from the radical is enhanced by tunnelling so with high doping the electron injection is preferred.

Preliminary measurements have been initiated on the oxidation of alkenes and alkanes by holes from TiO_2 and SnO_2.

Highly acid solvents such as phosphoric acid and triflic acid (trifluoromethane sulfonic acid) have been examined. The results indicate most effective oxidation on tin oxide rather than TiO_2 but this is yet to be confirmed and the details are yet to be determined.

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